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(54) METHOD OF REMOVING ORGANIC HALIDE.

(57) A method of removing a halogenated organic compound such as carbon tetrachloride contained in an amount of about 10 to 10,000 ppm in a waste gas by decomposing the halide through contact with an acidic zeolite, optionally either subjected to ion exchange with metals of the second to sixth periods of the periodic table or supporting these metals thereon. It is possible to remove an organic halide even at a relatively low temperature of 100 to 400 °C and to dispose of also a hydrogen-free organic halide.

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## Technical field

The present invention relates to a decomposition method of organic halogenated substances. In more detail, it relates to a method of removing halogenated organic compounds containing at least one kind of chlorine, fluorine, bromine, etc. through catalytic decomposition.

## Background techniques

Organic halogenated substances such as Freon gas and trichloroethylene are excellent in their chemical properties, in particular, as solvents, jet chemicals, refrigerants, etc. and are most often used in general as well as in industrial world.

These substances however have high volatility commonly and such problems as the destruction of ozonosphere, promotion of global warming and carcinogenicity are pointed out when emitted into the atmosphere as exhaust gases. Hence, recently, the measures are proposed as urgent themes from the aspect of environmental maintenance. In particular, with respect to a part of organic halogenated substances, limitation of their use is decided in the "Protocol on the substances destroying the ozonosphere in Montreal". The measures for the regulation of emission include recovery method, decomposition method, etc. after collected these at the time of emission.

As the collection or decomposition method of organic halogenated substances, there is commonly a method of adsorbing these onto active charcoal or active carbon fibers to recover. This method shows relatively high adsorption effect when the concentration of adsorbing substance is high, but the efficiency becomes poor, when said concentration is low, i.e. the partial pressure is low, since the adsorption level is low and further the adsorption of organic halogenated substance is often obstructed by other coexisting substances. In addition, there is a problem that active charcoal burns, if the heating temperature is too high (over 200 °C) at the time of recovery. Moreover, as the decomposition method, there is a thermal decomposition method. This method includes a method of thermally decomposing at high temperature, e.g. 800 °C and a method of thermally decomposing adsorbed substance on active charcoal at a temperature of up to 800 °C in nitrogen stream. With the latter method, however, if treating, for example, chlorofluorocarbons (CFC-11, CFC-12, etc.) as halogenated substances, carbon tetrachloride is produced, which is not decomposed further at a temperature below 800 °C. Further, while the thermal decomposition method is a relatively inexpensive decomposition method, it imposes secondary problems that halogen freed by decomposition corrodes the material of decomposition device, and the like.

Furthermore, a decomposition method with reductive reagent through chemical reaction has also been investigated and the reagent that is inexpensive and selectively decomposes the decomposing substance is searched diligently. In recent, with respect to the regulated Freon having high potential to destroy the ozonosphere, the development of alternative Freon not causing the destruction of ozonosphere is conducted vigorously. With these alternatives, the problem on the ozonosphere in stratosphere can be solved, but they decompose by themselves in the atmosphere being lower layer, leading to a potential causing new atmospheric pollutions such as acid rain. Hence, it is required to control the emission of organic halogenated substances into the atmosphere, regardless of whether they may be already existing products or alternatives, and the establishment of decomposition techniques of said compounds at the generating sources is of importance. It is considered that, for the method of decomposing and removing organic halogenated substances particularly from the aspect of environmental maintenance, at least following matters are satisfied. Namely,

- 1) The decomposition should be surely possible under broad manipulative conditions.
- 2) The generation of detrimental by-products resulting from the decomposition should be inhibited.
- 3) The treating substance should be selectively decomposable in the mixture containing treating substance.
- 4) The correspondence should be possible properly to the emitting form of treating substance, and so forth.

As a result of the investigations on various methods for the purpose of providing a method of decomposing organic halogenated substances adapting to the problems above, the inventors have found a simple and efficient method, leading to the completion of the invention.

## Disclosure of the invention

The invention relates to a method of removing organic halogenated substances characterized by contacting one or more kinds of metal compounds selected from a group consisting of metals belonging to

the third period through the sixth period in the periodic table excluding IA group and IIA group elements in said table and compounds having on or more kinds of these metals as metal species with organic halogenated substance to decompose this, and the invention is characterized by contacting acid zeolite with a gas containing halogen-containing organic compound and relates to a treatment method using, in particular, acid zeolite carrying and/or substituted with one or more kinds of metals belonging to the second period through the sixth period in the periodic table.

In following, the invention will be illustrated in detail.

The organic halogenated substances intended for the treatment in the invention are compounds having relatively low molecular weight and having carbon atoms combined with one or more kinds of halogen atoms such as chlorine, fluorine and bromine. Concretely, they include trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113), bromotrifluoromethane, carbon tetrachloride, trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane and so forth. The molecular diameter of these compounds is about 7.5 Å at maximum.

The feature of the invention is to contact these organic halogenated substances with metal compounds. Moreover, additional organic halogen compounds intended for the treatment in the invention are mainly compounds with molecular diameter of not more than 7.5 Å, though they are not particularly restricted, for example, halogenated methane, halogenated ethane, halogenated propane, halogenated ethylene, halogenated propylene, chloroprene, halogenated cyclobutane, halogenated cyclohexane, halogenated benzene, halogenated toluene, halogenated styrene and so forth, and the method of the invention is particularly suitable for the treatment of organic halogen compounds with carbon atoms of not more than 6 such as methane fluoride, chloromethane, methane bromide, methane iodide, carbon tetrachloride, vinyl chloride, allyl chloride, chloropropane, chloroprene, benzene chloride, etc. And, in the invention, gases such as waste gas containing these are treated.

The metal species of the first metal compounds to be used in the invention belong to the third period through the sixth period in the periodic table excluding the elements belonging to IA and IIA in the same table.

These metal compounds are crystalline oxides, noncrystalline oxides, chlorides, sulfates, complexes and so forth of one or more metal species such as Al, Si, V, Fe, Co, Cu, Zn, Zr, Mo, Pd, Pt, Ag and Hg, and one kind or mixtures of these are used. Moreover, usually, these compounds are used by carrying on the carriers used for the carriers of catalysts, for example, later-describing zeolite, silica, alumina, clay mineral, silica-alumina, silica-titania, etc. or also by ion-exchanging with metal ions of metal species constituting these metal compounds. Mixing combination and mixing proportion on using said mixtures are not particularly restricted.

Moreover, the proportion when carrying on (or ion-exchanging) the carrier is 0.1 to 50 wt. % as metal based on the weight of carrier. Furthermore, the carrying (or ion-exchanging) can be performed by general methods. Namely, a method of contacting aqueous solution containing intending ingredient with carrier followed by drying etc. and a method of kneading after mixed both are included.

As the second metal compounds to be used in the invention, aluminosilicate and/or aluminophosphate can be mentioned.

The aluminosilicate is constituted with  $\text{SiO}_4$  tetrahedron and  $\text{AlO}_4$  tetrahedron and many types are known depending on the existing ratio of Si to Al and the difference in the bonding mode of each tetrahedron. And, these constituents form a lattice of three-dimensional skeleton structure producing the caves (pores) in lattice. These caves afford the adsorptive function that features zeolite to zeolite and the magnitude thereof takes various values depending on the ratio of constituents and the skeleton structure.

The zeolite to be used in the invention is that having larger pore diameter than the molecular diameter of organic halogenated substances aforementioned, and, as the zeolites satisfying this condition, for example, faujasite type, mordenite type, L type, omega type, ferrierite type, ZSM-5 type and so forth are all suitable. In the invention, said zeolites can be used in the state as they are, but zeolites in which the ion-exchangeable components of constituents of these zeolites have been ion-exchanged with other cations ion-exchangeable therewith, for example, zeolites ion-exchanged with transition metal ions, alkali metal ions, alkaline earth metal ions, rare-earth metal ions, ammonium ions or protons, zeolites carrying other ingredients, for example, said metals, their complexes, chlorides, nitrates, hydroxides, oxides, etc. making then as carriers, and further mixtures of said ingredients with zeolites, and the like are also used.

The ion-exchanging and carrying as described above can be performed by general methods. Namely, a method of contacting aqueous solution containing intending ingredient with zeolite followed by drying etc. and a method of kneading after mixed both are included. The content of these ingredients when allowing to contain into zeolite is 0.1 to 50 wt. %, preferably 0.1 to 20 wt. % based on zeolite.

On the other hand, aluminophosphate has a resemblant skeleton structure to zeolite and the com-

positing with metals (carrying or mixing with metals) on using in the invention can be performed by similar methods to the case of said zeolite.

In the invention, by using said zeolite as acid type, the organic halogen compounds can be decomposed more efficiently.

5 Here, one method of making acid zeolite is to contact zeolite with aqueous solution containing ammonium ions (aqueous solutions of  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ , etc.) to convert to ammonium-ion type zeolite and then to calcine it at a temperature of not lower than  $300^\circ\text{C}$  to convert to H type zeolite by eliminating ammonia. Moreover, other method is to contact with strong acids such as  $\text{HCl}$  to convert to H type zeolite by directly ion-exchanging with H ions. Since the H type zeolites thus prepared show acidic character, they  
10 are called acid zeolites.

In the treatment method of the invention, hydrogen halides such as  $\text{HCl}$  are generated in the process of the treatment as describing later. Among zeolites, those having such composition that the molar ratio of Si to Al (Si/Al) constituting the zeolite is under 3 are weak against acid and the crystals are easily broken by  $\text{HCl}$ ,  $\text{HF}$ , etc. to lose the function as catalysts. Hence, it is not preferable to use zeolites with low Si/Al molar  
15 ratio in the invention and the use of zeolites with the ratio of not less than 3 is preferable. As one of the methods to increase the Si/Al molar ratio of zeolite, there is a method of heating ammonium-ion type zeolite at a temperature of not lower than  $400^\circ\text{C}$  under the atmosphere of steam, which is a method to be used usually for the de-Al of faujasite type zeolite. Moreover, there is a method of contacting  $\text{SiCl}_4$  with zeolite under the condition of absence of steam. This is a method of substituting Al with Si and has an advantage  
20 that no lattice defects produced by pulling-out of Al atoms generate in zeolite. In addition, there are a method of using chelating agents such as ethylenediamine-tetraacetic acid and a method of using acids such as hydrochloric acid. In the invention, zeolites with inherently high Si/Al molar ratio and those obtainable by all of said methods can be applied.

Such acid zeolites can be used for the invention in the form as they are, but, by using zeolites carrying  
25 and/or substituted with one or more kinds of metals, the organic halogen compounds can be treated preferably. The metals to be used here are one or more kinds of metals belonging to the second period through the sixth period in the periodic table and, in particular, transition metals such as V, Fe, Co, Ni, Zn, Zr, Mo, Nb, Pd, Pt and Ag are effective. The carrying and substituting methods of metals at this time are not particularly restricted, and, for example, a method of contacting H type zeolite with aqueous solution  
30 containing said metals followed by removal of solution, washing and drying, a method of impregnating H type zeolite with said aqueous solution followed by drying, and the like are included. The amount of metal to be used here is 0.1 to 50 wt. %, preferably 0.1 to 20 wt. % based on zeolite. Moreover, when performing the metal substitution through ion-exchange, it is preferable to leave behind the acid in amounts of not less than 50 % to those before ion-exchange from the aspects of activity etc.

35 The actual use form of metals or metal compounds used in the invention may be powdery, or may be any of moldings molded by usual method, crushed products thereof and the like. Moreover, the size of these on using differs depending on the use scale thereof, but the diameter of granulated products on granulating is preferable to be 0.2 to 10 mm.

In the invention, the method of contacting organic halogenated substance with said metal compounds  
40 may be either in gas phase or in liquid phase, but, from the points of properties of treating substance, e.g. high volatility etc., it is preferable to conduct in gas phase. Namely, this is a method of introducing gas containing organic halogenated substance into a bed packed with powdery, granular or pelletal metal compounds or a bed made honeycomb-shaped. The contact temperature at this time is room temperature or higher ranging preferably from  $100$  to  $800^\circ\text{C}$ , more preferably from  $150$  to  $600^\circ\text{C}$ . Moreover, the  
45 amount of organic halogenated substance in gas to be introduced into the bed of catalyst is 0.1 ppm to 100 %, preferably 10 to 10000 ppm. The introducing proportion (space velocity, SV) of this gas containing organic halogenated substance into the bed of catalyst is not more than  $100,000\text{ h}^{-1}$ , preferably not more than  $50,000\text{ h}^{-1}$ . Furthermore, if the decomposition treatment in the invention is performed in the presence of moisture in reaction system, the moisture reacts with organic halogenated substance to produce carbon  
50 dioxide, carbon monoxide and hydrogen halide, which is preferable for the disposal of treated substance in subsequent process. For the amount of water to be used at this time, it is preferable to use an amount of not less than the stoichiometric amount sufficient to produce carbon dioxide, carbon monoxide and hydrogen halide through the reaction of organic halogenated substance with water. Moreover, the components other than the foregoing in the treating gas are not particularly restricted. In the components after the decomposition treatment in the invention, hydrogen halide etc. are sometimes contained, which can be  
55 removed by contacting with alkalies such as sodium hydroxide, potassium hydroxide, calcium hydroxide, ammonia and amine.

Moreover, when carbon monoxide is contained, it can be converted easily to carbon dioxide by using

oxidation catalyst.

Best embodiment for practicing the invention

5 In following, the invention will be illustrated in more detail using examples.

#### Example 1

A gas containing 0.1 vol. % of chlorofluorocarbon (CFC-113) and 0.1 vol. % of moisture (other  
10 component: dry air) was used as a treating gas.

The catalyst used was  $\gamma$ -alumina. This was molded, arranged to the particle size of 0.2 to 0.6 mm diameter and 1 g thereof was packed in a quartz reaction tube with a diameter of 12 mm and a length of 150 mm for use. The treating gas was introduced into this reaction tube at a reaction temperature of 500 °C and at 500 ml/min for decomposition treatment. The reaction was continued for 50 hours in total and the  
15 reaction products after 10 hours and 50 hours from the beginning of reaction were analyzed by means of gas chromatographic method (column: packed with Chromosolve-102, column temperature: 150 °C). As the products containing carbon, components other than CO<sub>2</sub> and CO were hardly detected in the decomposition product. The decomposition rates of halogenated substance are shown in Table 1. Moreover, when the reaction product was treated by introducing into 0.2 N aqueous solution of NaOH, F<sup>-</sup> and Cl<sup>-</sup> ions were  
20 detected in the aqueous solution of NaOH, thus the generation of HF and HCl was confirmed through the decomposition reaction of treating gas in the reaction phase.

#### Example 2

25 Except that ferric oxide was used as a catalyst, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 1. In this example, too, as the products containing carbon, components other than CO<sub>2</sub> and CO were hardly detected in the decomposition product. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

#### Example 3

30 Except that a catalyst carrying 10 wt. % of cobalt was used as a catalyst by contacting silica with aqueous solution of cobalt chloride, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 1. In this example, too, as the products containing carbon, components other than CO<sub>2</sub> and CO were hardly detected in the decomposition product. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

#### Example 4

40 Except that a catalyst carrying 10 wt. % of cobalt was used as a catalyst by contacting kaolinite with aqueous solution of cobalt chloride, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 1. In this example, too, as the products containing carbon, components other than CO<sub>2</sub> and CO were hardly detected in the decomposition product. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

#### Example 5

50 Except that the reaction temperature was made to be 400 °C in Example 1, the reaction and the analysis were conducted under the similar conditions to Example 1. Results are shown in Table 1.

#### Example 6

55 Except that SiO<sub>2</sub>-TiO<sub>2</sub> (SiO<sub>2</sub>/TiO<sub>2</sub> molar ratio 1.54) was used as a catalyst, the reaction and the analysis were conducted under the similar conditions to Example 1. Results are shown in Table 1. In this example, too, as the products containing carbon, components other than CO<sub>2</sub> and CO were hardly detected in the

decomposition product. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

#### Example 7

Into 500 ml of methanol were dissolved 16 g of  $\text{TiCl}_4$  and 10 g  $\text{ZrOCl}_2$ , and aqueous solution of ammonia (28 wt. %) was added to this solution until pH became to 7 to 8. The precipitates caused were filtered off and washed with pure water until  $\text{Cl}^-$  ions disappeared. Thereafter, they were dried at a temperature of 120 °C and calcined at 650 °C to convert to  $\text{TiO}_2\text{-ZrO}_2$ .

Except that this  $\text{TiO}_2\text{-ZrO}_2$  was used, the reaction and the analysis were conducted under the similar conditions to Example 1. Results are shown in Table 1. In this example, too, as the products containing carbon, components other than  $\text{CO}_2$  and CO were hardly detected in the decomposition product. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

#### Example 8

Except that a catalyst containing 5 wt. % of copper ions obtained by contacting  $\text{TiO}_2\text{-ZrO}_2$  prepared in Example 7 with aqueous solution of copper nitrate for ion-exchange was used, the reaction and the analysis were conducted under the similar conditions to Example 1. Results are shown in Table 1. In this example, too, as the products containing carbon, components other than  $\text{CO}_2$  and CO were hardly detected in the decomposition product. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

#### Example 9

Ten g of  $\gamma$ -alumina were impregnated with 2 g of boric acid and this was dried at 120 °C and then calcined at 500 °C to obtain  $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ . Except that this  $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$  was used as a catalyst, the reaction and the analysis were conducted under the similar conditions to Example 1. Results are shown in Table 1. In this example, too, as the products containing carbon, components other than  $\text{CO}_2$  and CO were hardly detected in the decomposition product. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

Table 1

Decomposition rate (%) of CFC-113		
	After 10 hrs.	After 50 hrs.
Example 1	85	87
Example 2	68	65
Example 3	72	74
Example 4	75	77
Example 5	72	70
Example 6	56	54
Example 7	95	93
Example 8	98	96
Example 9	86	83

#### Example 10

A gas containing 0.1 vol. % of chlorofluorocarbon (CFC-113) and 0.4 vol. % of moisture (other component: dry air) was used as a treating gas.

Zeolite used was faujasite type zeolite (made by Tosoh Corp., trade name "NSZ-310-NAA", pore diameter about 8 Å) and one with an average particle diameter of about 10  $\mu\text{m}$  was contacted with aqueous solution of cobalt chloride and ion-exchanged to convert to zeolite containing 16 wt. % of cobalt ions. This was molded, arranged to the particle size of 0.2 to 0.6 mm diameter and 1 g thereof was packed in a quartz reaction tube with a diameter of 12 mm and a length of 150 mm for use. The treating gas was introduced

into this reaction tube at a reaction temperature of 500 °C and at 500 ml/min for decomposition treatment. The reaction was continued for 50 hours in total and the reaction products after 10 hours and 50 hours from the beginning of reaction were analyzed by means of gas chromatographic method (column: packed with Chromosolve-102, column temperature: 150 °C). As the products containing carbon, components other than CO<sub>2</sub> and CO were hardly detected in the decomposition product. The decomposition rates of halogenated substance are shown in Table 2. Moreover, when the reaction product was treated by introducing into 0.2 N aqueous solution of NaOH, F<sup>-</sup> and Cl<sup>-</sup> ions were detected in the aqueous solution of NaOH, thus the generation of HF and HCl was confirmed through the decomposition reaction of treating gas in the reaction phase.

10

#### Example 11

Except that a zeolite containing 14 wt. % of cobalt ions obtained by contacting mordenite type zeolite (made by Tosoh Corp., trade name "HSZ 8600 NAA", pore diameter 7.5 Å) with aqueous solution of cobalt chloride for ion-exchange was used as a zeolite, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 2. In this example, too, as the products components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

20

#### Example 12

Except that a zeolite carrying 10 wt. % of palladium obtained by contacting faujasite type zeolite (made by Tosoh Corp., trade name "HSZ-310 NAA", pore diameter 8 Å) with aqueous solution of tetraminedichloropalladium was used as a zeolite, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The composition rates are shown in Table 2. In this example, too, as the products, components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

#### Example 13

Except that non-ion-exchanged faujasite type zeolite (made by Tosoh Corp., trade name "HSZ-310 NAA", pore diameter 8 Å) was used as a zeolite, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 2. In this example, too, as the products, components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

#### Example 14

40

Except that the reaction temperature was made to be 400 °C in Example 10, the reaction and the analysis were conducted under the similar conditions to Example 1. Results are shown in Table 2.

#### Example 15

45

Except that mordenite type zeolite (made by Tosoh Corp., trade name "HSZ-640 HOA", pore diameter 7.5 Å) was used as a zeolite, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 2. In this example, too, as the products, components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

#### Example 16

Except that faujasite type zeolite (made by Tosoh Corp., trade name "HSZ-320 HOA", pore diameter 8 Å) was used as a zeolite, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 2. In this example, too, as the products, components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

## Example 17

Except that a zeolite containing 5 wt. % of copper ions obtained by contacting mordenite type zeolite (made by Tosoh Corp., trade name "HSZ-640 HOA", pore diameter 8 Å) with aqueous solution of copper nitrate for ion-exchange was used as a zeolite, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 2. In this example, too, as the products, components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

## Example 18

Except that ZSM-5 type zeolite (made by Tosoh Corp., trade name "HSZ-840 HOA", pore diameter 7 Å) was used as a zeolite, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 2. In this example, too, as the products, components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

Table 2

Decomposition rate (%) of CFC-113		
	After 10 hrs.	After 50 hrs.
Example 10	82	85
Example 11	78	81
Example 12	76	79
Example 13	35	32
Example 14	68	71
Example 15	98	92
Example 16	82	76
Example 17	100	94
Example 18	79	76

## Example 19

Except that a zeolite containing 5 wt. % of copper ions obtained by contacting mordenite type zeolite (made by Tosoh Corp., trade name "HSZ-640 HOA", pore diameter 7.5 Å) with aqueous solution of copper nitrate for ion-exchange was used as a zeolite, dichlorodifluoromethane was used as an organic halogenated substance, and the reaction temperature was made to be 350 °C, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 3. In this example, too, as the products, components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

## Example 20

Except that a zeolite containing 5 wt. % of copper ions obtained by contacting mordenite type zeolite (made by Tosoh Corp., trade name "HSZ-640 HOA", pore diameter 7.5 Å) with aqueous solution of copper nitrate for ion-exchange was used as a zeolite, chlorotrifluoromethane was used as an organic halogenated substance, and the reaction temperature was made to be 550 °C, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 3. In this example, too, as the products, components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

## Example 21



Except that a zeolite containing 5 wt. % of copper ions obtained by contacting mordenite type zeolite (made by Tosoh Corp., trade name "HSZ-640 HOA", pore diameter 7.5 Å) with aqueous solution of copper nitrate for ion-exchange was used as a zeolite, tetrachloroethylene was used as an organic halogenated substance, and the reaction temperature was made to be 550 °C, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 3. In this example, too, as the products, components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

#### Example 22

Except that a zeolite containing 5 wt. % of copper ions obtained by contacting mordenite type zeolite (made by Tosoh Corp., trade name "HSZ-640 HOA", pore diameter 7.5 Å) with aqueous solution of copper nitrate for ion-exchange was used as a zeolite, trichloroethylene was used as an organic halogenated substance, and the reaction temperature was made to be 500 °C, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 3. In this example, too, as the products, components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

#### Example 23

Except that TiO<sub>2</sub>-ZrO<sub>2</sub> used in Example 7 was used, trichloroethylene was used as an organic halogenated substance, and the reaction temperature was made to be 500 °C, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 3. In this example, too, as the products, components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

#### Example 24

Except that a zeolite containing 5 wt. % of copper ions obtained by contacting mordenite type zeolite (made by Tosoh Corp., trade name "HSZ-640 HOA", pore diameter 7.5 Å) with aqueous solution of copper nitrate for ion-exchange was used as a zeolite, 1,1,1-trichloroethylene was used as an organic halogenated substance, and the reaction temperature was made to be 300 °C, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 3. In this example, too, as the products, components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

#### Example 25

Except that a zeolite containing 5 wt. % of copper ions obtained by contacting mordenite type zeolite (made by Tosoh Corp., trade name "HSZ-640 HOA", pore diameter 7.5 Å) with aqueous solution of copper nitrate for ion-exchange was used as a zeolite, carbon tetrachloride was used as an organic halogenated substance, and the reaction temperature was made to be 200 °C, the reaction was conducted under the similar conditions to Example 1. The reaction product was analyzed similarly to Example 1. The decomposition rates are shown in Table 3. In this example, too, as the products, components other than CO<sub>2</sub> and CO were hardly detected. Moreover, as a result of analysis by the similar method to Example 1, the generation of HF and HCl was confirmed.

Table 3

Decomposition rate (%) of organic halogenated substance		
	After 10 hrs.	After 50 hrs.
Example 19	95	92
Example 20	86	81
Example 21	98	96
Example 22	99	98
Example 23	97	98
Example 24	99	97
Example 25	100	100

## Example 26

H type mordenite type zeolite (made by Tosoh Corp., trade name "HSZ-640 HOA", Si/Al = 10) was used as a catalyst. One g thereof was packed in a quartz reaction tube with a diameter of 12 mm and a length of 150 mm, and a gas containing 0.1 vol. % of  $\text{CCl}_4$  as a halogen-containing organic compound and 1.0 vol. % of steam (other component: air) was introduced into this at a velocity of 500 ml/min as a treating gas, which was reacted at temperatures shown below. Besides, the analysis of treated gas was performed by means of gas chromatography. Results are shown below.

Treatment temp. (°C)	Decomposition rate (%)
150	68
200	97

## Example 27

Except that a zeolite containing 3 wt. % of cobalt ions obtained by contacting the zeolite used in Example 26 with 10 wt. % aqueous solution of cobalt nitrate for 2 hours at 80 °C for cobalt ion-exchange was used as a catalyst, treatment was made similarly to said example. Results are shown below.

Treatment temp. (°C)	Decomposition rate (%)
150	96
200	100

## Example 28

Except that a zeolite carrying 1 wt. % of Pd obtained by impregnating the zeolite used in Example 26 with aqueous solution of tetraminedichloropalladium was used, treatment was made similarly to said example. Results are shown below.

Treatment temp (°C)	Decomposition rate (%)
150	95
200	100

## Example 29 - 31

Treatment temp. (°C)	Decomposition rate (%)
150	89
200	100

#### Example 55

Except that a zeolite carrying 1 wt. % of Pd obtained by impregnating H type Y type zeolite (made by Tosoh Corp., trade name "HSZ-330 HSA", Si/Al=3) with aqueous solution of tetraminedichloropalladium was used, treatment was made similarly to Example 26. Results are shown below.

Treatment temp. (°C)	Decomposition rate (%)
150	84
200	100

Besides, the decomposition rate was determined from following amounts per unit time.

A: Amount of organic halogenated substance introduced

B: Amount of organic halogenated substance unreacted

$$\text{Decomposition rate} = (A - B)/A \times 100$$

#### Utilization potential in the industry

The invention provides a simple method and also allows a simple manipulation, thus making it possible to utilize it not only for a large-scale equipment for processing in large quantities, but also for a small-scale equipment for processing in small quantities. Moreover, through the decomposition of organic halogenated substances, less decomposition products difficult for treatment and less detrimental by-products difficult for collection are produced in subsequent process resulting in no generation of secondary environmental pollution by this method.

Moreover, the zeolite to be used in the invention is acid-resistant and has high activity making it possible to treat at a lower treatment temperature compared with the conventional method. Moreover, it is possible to easily treat the organic halogen compounds containing no hydrogen.

#### Claims

1. A method of removing organic halogenated substances characterized by contacting metal compound with organic halogenated substance to decompose it.
2. The method of Claim 1, wherein the metal compound comprises one or more kinds selected from a group consisting of metals belonging to the third period through the sixth period in the periodic table excluding IA group and IIA group elements in said table and metal compounds having one or more kinds of these metals as metal species.
3. The method of Claim 1 characterized by contacting organic halogenated substance with aluminosilicate (zeolite) and/or aluminophosphate having a pore diameter larger than the molecular diameter of said organic halogenated substance.
4. A treatment method of gas containing organic halogen compound characterized by contacting gas containing organic halogen compound with acid zeolite.
5. The treatment method of Claim 4, wherein the acid zeolite is an acid zeolite carrying and/or substituted with metal.
6. The treatment method of Claim 5, wherein the carrying and/or substituting metal comprises metals belonging to the second period through the sixth period in the periodic table.

7. The treatment method of any of Claim 4 through 6, wherein the acid zeolite is a zeolite having Si/Al ratio of not less than 3.
8. The method of any of Claim 1 through 7, wherein the organic halogenated substance is a compound containing at least one kind of fluorine, chlorine, bromine and iodine.

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## Example 42 - 46

Using a gas containing  $\text{CH}_2\text{Cl}_2$  as a treating gas and further using zeolite treated similarly to Example 27 so as the zeolite used in said example to contain Co (Example 43), Cu (Example 44), Ni (Example 45) or Fe (Example 46) and untreated zeolite (Example 42), treatment was made similarly to Example 26. Results are shown below.

	Example	Metal ion	Treatment temp. (°C)	Decomposition rate (%)
10	42	None	350	43
		"	400	84
15	43	Co	350	56
		"	400	98
20	44	Cu	350	58
		"	400	100
25	45	Ni	350	49
		"	400	91
	46	Fe	350	51
30		"	400	90

## Example 47 - 51

Using a gas containing  $\text{CH}_2\text{ClCH}_2\text{Cl}$  as a treating gas and using respective zeolite used in Example 32 - 36 (Co: Example 48, Cu: Example 49, Ni: Example 50, Fe: Example 51, no metal ion-exchange: Example 47), treatment was made similarly to Example 26. Results are shown below.

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	Example	Metal ion	Treatment temp. (°C)	Decomposition rate (%)
5	47	None	250	41
		"	300	92
	48	Co	250	73
10		"	300	94
	49	Cu	250	96
15		"	300	99
	50	Ni	250	58
		"	300	90
20	51	Fe	250	91
		"	300	99

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## Example 52

30 Except that a zeolite containing 3 wt. % of Co ions obtained by contacting H type ZSM-5 type zeolite (made by Tosoh Corp., trade name "HSZ-820 HOA", Si/Al=11) with aqueous solution of cobalt chloride was used, treatment was made similarly to Example 26. Results are shown below.

35	Treatment temp. ( ° C)		Decomposition rate (%)
	150		40
	200		80

## 40 Example 53

45 Except that a zeolite containing 3 wt. of cobalt ions obtained by contacting H type Y type zeolite (made by Tosoh Corp., trade name "HSZ-330 HSA", Si/Al=3) with aqueous solution of cobalt chloride was used, treatment was made similarly to Example 26. Results are shown below.

50	Treatment temp. (°C)		Decomposition rate (%)
	150	66	
	200	89	

## 55 Example 54

Except that a zeolite carrying 1 wt. % of Pd obtained by impregnating H type ZSM-5 type zeolite (made by Tosoh Corp., trade name "HSZ-820 HOA", Si/Al=11) with aqueous solution of tetraminedichloropalladium was used, treatment was made similarly to Example 26. Results are shown below.

Except that a zeolite containing about 3 wt. % of Cu (Example 29), Ni (Example 30) or Fe (Example 31) obtained by contacting with aqueous solution containing them, respectively, similarly to Example 27 was used, treatment was made similarly to Example 26. Results are shown below.

Example	Metal ion	Treatment temp. (°C)	Decomposition rate (%)
29	Cu	150	87
	"	200	100
30	Ni	150	76
	"	200	99
31	Fe	150	81
	"	200	100

#### Referential example

Except that cobalt ion-exchanged zeolite obtained by contacting Na type Y type zeolite (made by Tosoh Corp., trade name "HSZ-310 NAA", Si/Al=2.5) with aqueous solution of cobalt nitrate was used as a catalyst, treatment was made similarly to Example 26. Results are shown below.

Treatment temp. (°C)	Decomposition rate (%)
200	2
250	11
300	56

#### Example 32-36

Using a gas containing  $\text{CHCl}_3$  as a treating gas and further using zeolite treated similarly to Example 27 so as the zeolite used in said example to contain Co (Example 33), Cu (Example 34), Ni (Example 35) or Fe (Example 36) and untreated zeolite (Example 32), treatment was made similarly to Example 26. Results are shown below.

	Example	Metal ion	Treatment temp. (°C)	Decomposition rate (%)
5	32	None	200	53
		"	250	95
10	33	Co	200	74
		"	250	100
	34	Cu	200	87
15		"	250	100
	35	Ni	200	80
20		"	250	100
	36	Fe	200	77
		"	250	99

## Example 37 - 41

30 Except that a gas containing  $\text{CH}_3\text{Br}$  was used as a treating gas and further a zeolite containing 5 wt. % of metal by impregnating the zeolite used in Example 26 with aqueous solution containing 5 wt. % of Pd (Example 37), Au (Example 38), Cr (Example 39), W (Example 40) or Cu (Example 41), respectively, was used, treatment was made similarly to example 26. Results are shown below.

	Example	Metal ion	Treatment temp. (°C)	Decomposition rate (%)
35	37	Pd	300	34
40		"	350	82
	38	Au	300	28
45		"	350	77
	39	Cr	250	48
		"	300	98
50	40	W	300	27
		"	350	83
55	41	Cu	250	56
		"	300	99



# INTERNATIONAL SEARCH REPORT

International Application No PCT/JP91/00258

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>4</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl <sup>5</sup> B01D53/36, 53/34		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC	B01D53/36, 53/34	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>4</sup>		
Jitsuyo Shinan Koho 1926 - 1991 Kokai Jitsuyo Shinan Koho 1971 - 1991		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>6</sup></b>		
Category <sup>8</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	JP, A, 52-7370 (Asahi Glass Co., Ltd.), January 20, 1977 (20. 01. 77), (Family: none)	1-8
X	JP, A, 62-273039 (Kanto Denka Kogyo Co., Ltd.), November 27, 1987 (27. 11. 87), (Family: none)	1, 2, 8
X	JP, A, 53-22864 (PPG Industries Inc.), March 2, 1978 (02. 03. 78) & US, A, 4039623 & DE, A1, 2736363 & GB, A, 1548357 & FR, A1, 2361929 & CA, A, 1075881	1, 2, 8
X	JP, A, 50-92878 (Sumitomo Chemical Co., Ltd.), July 24, 1975 (24. 07. 75), (Family: none)	1, 2, 8
X	JP, A, 51-147469 (Asahi Glass Co., Ltd.), December 17, 1976 (17. 12. 76), (Family: none)	1, 2, 8
<p><sup>9</sup> Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"8" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
April 11, 1991 (11. 04. 91)	April 22, 1991 (22. 04. 91)	
International Searching Authority	Signature of Authorized Officer	
Japanese Patent Office		

